

Fluoride Content and Liberation from Dental Cements and Filling Materials

THÈSE

présentée à la Faculté de médecine de l'Université de Genève
pour obtenir le grade de docteur en médecine dentaire

par

MICHEL LEGRAND

de Lausanne

Thèse n° 317

ZÜRICH
IMPRIMERIE BERICHTHAUS
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À MON PÈRE ET À MA MÈRE †

À MA CHÈRE FEMME

Fluoride Content and Liberation from Dental Cements and Filling Materials ♦

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Abstract.—A fluoride analysis was made in the powders and liquids of Achatit, Syntrex, TD 71, Addent, Concise, Adaptic, Kryptex, OIS adhesive, De Trey's zink cement, SS-White, Durelon, Dropsine, Kalsogen. For the powders, the procedure included an alkaline fusion, a distillation and the determination with an F^- -sensitive electrode. The powders of the first three filling materials and of Kryptex were found to contain concentrations of F^- higher than 10%. The other preparations contained a much lower amount and, in most of the cases, only traces of the halide. The liberation of fluoride in an aqueous *in-vitro* system followed, between 1 and 5 days after setting, a typical exponential pattern. The same was observed for some preparations supplemented with 2% NaF. The liberation of F^- generally reached zero at the fifth day of incubation, with the exception of Kryptex and of Dropsine supplemented with fluoride, both of which were found to liberate the halide for much longer periods of time.

Key words: Fluoride and dental fillings

INTRODUCTION

It is generally admitted that the incidence of recurrent carious lesions is low around the silicate restorations. VOLKER, BELKAKIS and MILILLO [12] have compared the frequency of carious lesions around silicate and amalgam fillings and found significantly less recurrent decays around the silicates. The same problem has been studied by LASWELL [4] in a large number of Navy recruits: this investigator observed that 9.2% of the amalgam and 8% of the resin fillings showed recurrent caries, whereas this happened only with 3.8% of the silicates.

By exposing the enamel surface of a series of teeth to silicate and to other fluoride containing compounds, PHILLIPS and SWARTZ were able to show that these materials induce a significant decrease of enamel solubility [10]. A definite influence on solubility was also confirmed by the same investigators in their study with powdered enamel [10].

That the effect on enamel solubility is caused by the uptake of fluoride was shown in the same laboratory by NORMAN, PHILLIPS and SWARTZ using powdered enamel [8] and by NORMAN,

PLATT, PHILLIPS and SWARTZ using intact enamel surfaces [9]. More recently, HALLSWORTH and WEATHERELL have analyzed the fluoride content of dentine and enamel surrounding a silicate filling in an extracted tooth. Their *in-vivo* observation confirmed that the hard dental tissues immediately surrounding such a restoration contain significantly more fluoride when compared to more distant enamel and dentine sites [3].

Although the action of fluoride upon the enzymatic machinery of the dental plaque cannot be excluded [1, 7], in view of the above findings and considerations, it is probable that the low incidence of recurrent caries around silicate fillings can be explained by the increased resistance of the surrounding tooth structure to acid attack.

Surprisingly, with the exception of a passing reference to the high fluoride content of silicates [3], little can be found in the literature on the actual fluoride amount contained in the commonly used dental cements and restoration materials.

MATERIAL AND METHODS

The materials analyzed

Fluoride was determined in the powders, pastes and liquids of the following dental restorations and cementing preparations, cavity liners and bases filling materials:

Esthetic restorations

- Achatit (Vivadent, Schaan/Liechtenstein)
- Syntrex (De Trey Frères SA, Zurich)
- "TD 71" (Dental Fillings Ltd., London)
- Addent (3 M)
- Concise (3 M)
- Adaptic (Johnson and Johnson, New Brunswick)

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Cementing preparations

- Kryptex (SS-White Co., Philadelphia)
- OIS adhesive system (Ortho Intern. Serv. Inc., San Francisco)
- De Trey's zink cement (De Trey Frères SA, Zurich)
- SS-White (SS-White Mfg Co., Philadelphia)

Cavity liners and bases

- Durelon (Espe Hersching Seefeld/Oberb.)
- Dropsine (Svedia-industr., Enköping)
- Kalsogen (De Trey Frères SA, Zurich)

Fluoride analysis

Fluoride analysis in the highly insoluble powders and pastes was started by an alkaline fusion followed by the procedure of separation of foreign ions through distillation and finally by the actual determination of the fluoride ion concentration.

For the alkaline fusion 0.5 to 1.0 g samples of powder or paste was mixed with 4.0 g of NaOH in a nickel cup and the mixture was heated on a bunsen flame at about 600 °C for 45 min. After cooling to room temperature, the fused material was dissolved in 7.5 ml of bi-distilled water.

Separation of fluoride ions was performed both by microdiffusion in modified plastic Conway cups [11] and by distillation. Only the latter technique gave consistent results. For the distillation, the method of WILLARD and WINTER was used, according to the description of MEGREGIAN and SOLET [5]. After the alkaline fusion, the dissolved material (7.5 ml) was transferred in the distillation chamber and the nickel cup was washed with 6 ml of bidistilled water. To this solution, 10 ml of sulfuric acid diluted 1:1 were added, followed by the slow adding of 22.5 ml of concentrated sulfuric acid. The distillation chamber was brought to a temperature of 150 °C by an electric heater, while the vapor generator was heated by a bunsen flame. The distillation temperature was maintained between 140 and 155 °C during 40 min, allowing the collection of 150 ml of distillate.

Finally, for the actual determination of the fluoride ions an Orion fluoride electrode was used, model 94-09. Prior to determination, all samples were diluted 1:2.5 with TISAB (Total ionic strength adjustment buffer).

The fluoride content of the liquids was determined with the Orion electrode after distillation of suitable samples. Each powder, paste and liquid were analyzed 6 times.

In-vitro liberation of fluoride

To study the pattern of liberation of fluoride from the dental materials, blocks were prepared in gelatin capsules having a volume of about 2 cc. Each capsule was opened after 24 h of setting and each block placed in a polyethylene flask containing 25 ml of physiological saline. Liberation of the halide ion was studied for the following incubation times: 2, 4, 6 and 15 h, 2, 10, 50 and 100 days. Sixteen blocks were prepared for each material, the experiment being performed in duplicate: at the end of each incubation time, the fluoride content of the two corresponding flasks was analyzed, respectively in 0.5 and 1 ml samples of saline.

This part of the study was performed for all the materials listed above. Where the analysis demonstrated little or no fluoride, 2% of sodium fluoride was added to the powders before mixing, and fluoride liberation was also determined on these samples.

RESULTS

Fluoride content of the materials analyzed

The fluoride contents in the powders (or pastes) of the various dental materials tested are given in Table I and are shown graphically in Figure 1. The esthetic restorations were separated into two categories, according to the chemical nature of the compound: the silicates and the composites.

As one could expect, the silicates (Achatit and Syntrex) were found to contain very high concentrations of fluoride. The composite TD 71 also revealed a fluoride content as high as 180000 ppm, this being true for both the powder and the liquid. As for the cements, the powder of Kryptex showed a fluoride content of about 110000 ppm, while the powders of OIS and de Trey were found to contain 3000 to 4000 ppm of the halide.

Interestingly, all the cavity liners and bases revealed a very low fluoride content. Finally, with the exception of TD 71, all the liquids of the preparations analyzed contained only traces of fluoride.

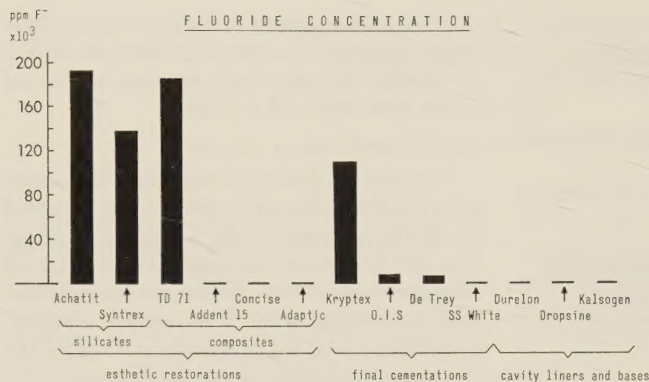


Fig. 1 A graphic representation of the fluoride content of various dental materials

In-vitro liberation of fluoride

The liberation of fluoride, with measurements starting 24 h after mixing the powder with the liquid, occurred very rapidly in the first few hours of incubation, and decreased progressively toward zero after about 2 days. This was the case for all the preparations tested, both the materials with an original high fluoride content and the preparations supplemented with 2% NaF. Some of these results are presented in Figures 2 and 3, with the abscissae showing, on a logarithmic scale, the time of incuba-

tion (in h) and the ordinate axis showing the fluoride liberated, as a percentage of the concentration found in the saline solution after the first 2 h of incubation.

Syntrex, Achatit and the highly fluoridated composite TD 71 showed a very similar pattern of fluoride liberation (Fig. 2). Kryptex, a cementing substance also containing a high amount of the halide, showed a similar exponential feature of fluoride diffusion but, in this case, fairly high concentrations could still be found in the flasks corresponding to 15, 48 and even 240 h of incubation.

The results concerning some of the materials originally containing only traces of fluoride and which were supplemented with 2% NaF are shown in Figure 3. The pattern of fluoride liberation for fluoridated Addent, SS-White and Kalsogen was very similar when compared with the preparations originally containing fluoride (Fig. 2). The same was true for Concise, Adaptic and Durelon. However, Dropsine, a widely used cavity liner, seemed to liberate its supplement of fluoride more slowly than any other material tested: Indeed, after 1200 h (50 days) of incubation, a measurable amount of fluoride could still be found in the liquid surrounding this block (Fig. 3).

DISCUSSION

It is probable that the lack of precise information about the fluoride content of dental filling materials is in part due to the technical difficulties that one encounters when trying to perform fluoride analyses in these compounds.

Table I Average fluoride concentration ($\pm$ St. Dev.) in various dental materials (ppm F) ($N = 6$)

<i>Esthetic restorations</i>		
Achatit		193 000 ($\pm$ 10 960)
Syntrex		138 700 ($\pm$ 8 250)
TD 71	< powder	187 400 ($\pm$ 28 700)
	< liquid	198 370 ($\pm$ 24 700)
Addent	< paste	39.9 ($\pm$ 22.9)
	< catalyst	59.3 ($\pm$ 19.8)
Concise	< paste	15.4 ($\pm$ 2.6)
	< catalyst	5.4 ($\pm$ 3.2)
Adaptic	< paste	53.3 ($\pm$ 2.5)
	< catalyst	12.5 ($\pm$ 2.5)
<i>Cementing preparations (final cementations)</i>		
Kryptex		113 400 ($\pm$ 5080)
OIS		3 900 ($\pm$ 570)
De Trey		3 100 ($\pm$ 110)
SS-White		45 ($\pm$ 5.8)
<i>Cavity liners and bases</i>		
Durelon		51.2 ($\pm$ 25)
Dropsine		61.4 ($\pm$ 17)
Kalsogen		54.0 ($\pm$ 18)

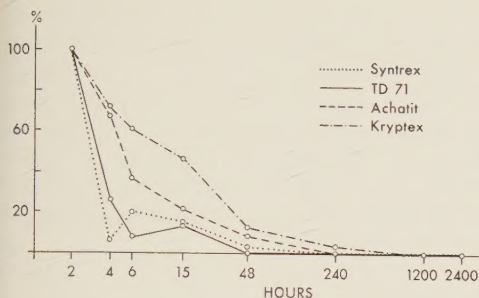


Fig. 2 The *in-vitro* pattern of fluoride liberation from 3 esthetic restorations and a cementing preparation containing a very high amount of fluoride. The fluoride concentration of the incubation flasks (abscissae) is expressed as the percentage of the concentration of halide found in the solution after the first 2 h of incubation

Dental cements and filling materials are highly insoluble and, as explained under Material and methods, an alkaline fusion was necessary to obtain a solution of the various powders or pastes analyzed. To separate fluoride from ions such as Si^{++} , Fe^{3+} , Al^{3+} , known to form complexes with the halide, two different procedures, distillation and diffusion, were attempted, but only the first gave consistent results. Finally, for the determination of the fluoride concentration in the distillate, the fluoride sensitive Orion electrode was successfully used.

This complex procedure is the likely explanation of the fairly high variability of the present results. Indeed, as shown in Table I, standard deviations sometimes as high as 50% of the

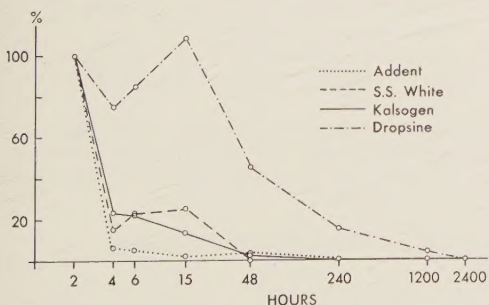


Fig. 3 The liberation of fluoride from some of the materials found to contain very little fluoride and which were supplemented with 2% NaF

average were found in the results of six repeated determinations.

As expected when considering the chemical nature of the material, the silicates were found to contain a very high amount of fluoride, and our results confirm the isolated data reported by HALLSWORTH and WEATHERELL [3]. The composites analyzed were found to contain very little fluoride. The cementing preparations, with the exception of Kryptex, and the cavity liners and bases also showed a low fluoride content.

Since it is established that dental hard tissues can acquire fluoride from a filling [3, 6, 8, 9], it is surprising that the manufacturers have not more often attempted to add fluoride salts to the common dental materials, the more so that the physical properties of such materials do not seem to be altered by this modification [2]. In this respect our *in-vitro* system has permitted some interesting observations. All the materials tested were found to liberate fluoride in the hours immediately following the beginning of the incubation. This liberation followed an exponential pattern and was practically finished after 48 h. Among the cementing preparations, Kryptex was found to liberate fluoride for a longer period of time. The materials supplemented with 2% NaF also showed an exponential pattern of fluoride liberation and, among those, Dropsine continued to liberate the halide up to 50 days after setting.

In general, the findings on the *in-vitro* fluoride liberation are in agreement with those of NORMAN *et al.* [8, 9]: this group studied fluoride release already after 1 h of setting and stopped their observations at 5 days. In dental filling materials and cements originally containing fluoride or supplemented with NaF, NORMAN and coworkers found that the greatest liberation of fluoride occurred during the first 24 h. They also reported that the amounts released diminished with time.

Although NORMAN *et al.* did not perform fluoride analysis of the materials tested in their laboratory, they based their calculations on the approximate amounts of fluoride salts employed by the manufacturer and were able to establish that only about 0.15% of the total amount present, for instance, in the silicate cement was

leached out in the five-days observation period. In view of the very high fluoride content of silicates and other filling materials this apparently small release of halide is however sufficient to explain the decrease of enamel solubility and, together with a possible action on dental plaque [1, 7], the low incidence of recurrent decays.

Zusammenfassung. Es wurde der Fluorgehalt in Pulver und Flüssigkeit von Achatit, Syntrex, TD 71, Addent, Concise, Adaptic, Kryptex, OIS-Adhesiv, De Trey-Zink-Zement, SS-White, Durelon, Dropsin und Kalsogen bestimmt. Die Fluorbestimmung in den Pulvern erfolgte mit der fluorspezifischen Elektrode nach vorausgegangen alkalischer Schmelzung und Dampfdestillation. Die ersten drei Füllungsmaterialien, ferner auch Kryptex, enthielten mehr als 10% Fluor. Die andern Präparate waren wesentlich fluorärmer, und in vielen Fällen enthielten sie nur Fluorspuren. Die Abgabe von Fluorionen in einem wässrigen In-vitro-System während 1-5 Tagen nach der Erhärtung der Füllung erfolgte exponentiell, bei allen Präparaten mit hohem Fluorgehalt und solchen, welchen 2% Natriumfluorid beigemischt worden war. Die Fluorabgabe erschöpfte sich ungefähr am fünften Tag, mit Ausnahme für Kryptex oder Dropsin + NaF. Letztere liberierten Fluor über noch längere Zeitabschnitte.

Résumé. Des analyses de fluor ont été faites dans les poudres et liquides des préparations suivantes: Achatit, Syntrex, TD 71, Addent, Concise, Adaptic, Kryptex, OIS adhesive, De Trey's zink cement, SS-White, Durelon, Dropsine, Kalsogen. Pour les poudres l'analyse du F^- au moyen de l'électrode spécifique Orion a été précédée d'une fusion alcaline et d'une séparation des ions gênants par distillation. Les poudres des trois premiers matériaux d'obturation et du Kryptex contenaient une concentration de fluor supérieure à 100000 ppm. Toutes les autres préparations contenaient beaucoup moins ou seulement des traces de F^- . Dans un système *in vitro*, il a été prouvé que la libération

de F^- , étudiée entre 1 et 100 jours, se fait de façon exponentielle durant les premiers 5 jours. La même chose a été observée pour les ciments dentaires pauvres en fluor, auxquels on a ajouté du fluorure de sodium à raison de 2% dans la poudre. Le Kryptex et la Dropsine (avec son supplément de NaF) semblent libérer l'ion fluor pendant des périodes de temps dépassant largement 5 jours.

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